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Growth of High Nitrogen Content GaAsN by Metalorganic Chemical Vapor Deposition

[1]J. C. Roberts, [2]B. F. Moody, [2]P. Barletta, [1]M. E. Aumer, [1]S. F. LeBoeuf, [1]J. M. Luther and [1]S. M. Bedair
[1]Dept. of Electrical & Computer Engineering, N. C. State University,
Campus Box 7911, Raleigh, N. C. 27695-7911.
[2]Dept. of Materials Science and Engineering, N. C. State University,
Campus Box 7907, Raleigh, N. C. 27695-7907

ABSTRACT

    The incorporation of a high percentage of nitrogen in the GaAs lattice has been the subject of recent interest to reduce the bandgap while maintaining the nearly lattice matched condition to GaAs. We will report on the metalorganic chemical vapor deposition (MOCVD) of GaAsN using trimethylgallium (TMG), tertiarybutylarsine (TBA) and dimethylhydrazine (DMHy) organometallic sources in a hydrogen-free carrier gas. A nitrogen concentration as high as ~8% in GaAsN was achieved. The effect of nitrogen concentration on the structural, optical and surface properties of GaAsN films will be discussed.

INTRODUCTION

    Recently, the $In_xGa_{1-x}As_{1-y}N_y$ material system has gained attention for use in optoelectronic devices [1,2,3]. The In and N mole fractions in this quaternary system can be chosen to maintain a lattice matching condition to GaAs while achieving a ~1eV bandgap, which is of interest for increasing the efficiency of tandem solar cells by using $In_xGa_{1-x}As_{1-y}N_y$ as the third layer in a standard GaAs/$Ga_{0.5}In_{0.5}P$ tandem solar cell [4]. The $In_xGa_{1-x}As_{1-y}N_y$ system is also becoming a primary material system for long wavelength laser diodes with excellent high temperature performance. However, only small nitrogen concentrations have been achieved by metalorganic chemical vapor deposition (MOCVD) of these materials due to the large miscibility gap. Several growth approaches have been applied to improve the nitrogen incorporation in this material system. High nitrogen content has been reported by using gas-source molecular beam epitaxy (GSMBE) in which radio frequency energy is used to generate active N species from an N_2 source [5]. Increases in N incorporation were achieved using dimethylhydrazine (DMHy) and replacing AsH_3 with tertiarybutylarsine (TBA). The lower cracking temperature of the column V organometallic sources DMHy and TBA allows lower temperature growth of GaAsN that can lead to higher nitrogen content [6]. The majority of research detailing the MOCVD growth of $GaAs_{1-y}N_y$ indicates the use of H_2 as the carrier gas, with nitrogen content as high as 5.6% reported [7]. In this work we will report that by substituting N_2 for H_2 as the carrier gas, nitrogen content in GaAsN as high as 8% can be achieved.

EXPERIMENTAL DETAILS

All materials were grown by MOCVD in a commercial Thomas Swan system equipped with a horizontal fused silica research reactor at pressures ranging from 700 torr to 1 atmosphere. Trimethylgallium (TMG) was used as the column III precursor, while TBA and DMHy were used as column V precursors. Column V organometallic sources were chosen not only for safety concerns, but also to take advantage of their lower cracking temperatures, which for the case of III-As-N related compounds, has been shown to result in enhanced nitrogen incorporation [8]. Ultra-high purity grade (99.999%) N_2 and H_2 were further purified with a resin-based scrubber and used as carrier gases with H_2 being varied from 0% to 67% of the total carrier gas flow. Semi-insulating GaAs substrates 2° off (100) toward [110] were solvent cleaned and then etched in a 7:1:1 solution of H_2SO_4, deionized water, and H_2O_2. After loading in the growth chamber, samples were cleaned for 5 minutes at 650° C under a TBA flux to desorb remaining surface contaminants. Typical growth temperatures ranged from 575°C to 650°C while the reactor pressure was always maintained at 700 torr. All sample temperature values refer to the reading taken from a K-type thermocouple inserted via a 1/4" quartz tube into the graphite susceptor. The actual sample temperature may not coincide exactly with that indicated by the thermocouple. The V/III ratio was 13 and the DMHy/(DMHy+TBA) ratio was 0.88 for all samples. GaAsN layers are nominally ~1μm thick with a ~70nm GaAs cap and were annealed *in situ* for 15 minutes at 675°C under N_2 at 700 torr immediately following deposition.

Alloy compositions were determined by examining the splitting between the (004) reflection peaks of GaAs and $GaAs_{1-y}N_y$ layers as determined from double-crystal x-ray diffraction (DCXRD) data. All $GaAs_{1-y}N_y$ layers were of sufficient thickness to be relaxed and the N content in the layers was determined by applying Vegard's Law using GaAs (a ≈ 5.65 Å) and cubic GaN (a ≈ 4.52 Å) as the binary end members. PL measurements were made at 77 K by mounting samples to a liquid nitrogen-cooled Cu plug with Crycon grease. The 514 nm line of an Ar ion laser was used to excite the PL signal, which was collimated, focused and dispersed through a 1/2 m monochromator and detected by a cooled photomultiplier tube. The nitrogen content measured for samples grown with H_2 as a large fraction of the carrier gas agrees well with nitrogen content reported in the literature for GaAsN samples grown under similar conditions. However, by increasing the ratio of N_2 to H_2, the amount of nitrogen incorporated into the film increased. The total flow through the reactor was always held constant, i.e., as the H_2 flow was reduced, the N_2 flow was increased to balance the flow.

DISCUSSION

Figure 1 illustrates the importance of two fundamental parameters, growth temperature and the presence of H_2 in the carrier gas, which influence the incorporation of nitrogen in GaAsN. Two sets of samples are shown here, one set (solid circles) grown with 50% H_2/50% N_2 as the carrier gas and the second set (solid squares) grown with no H_2 in the carrier gas (i.e., 100% N_2). We attribute the scatter in the data to several factors including some nonuniformity of nitrogen content due to lack of substrate rotation, organometallic depletion effects, and small run-to-run substrate temperature differences that can arise from variability of thermocouple placement. The

highest nitrogen content was achieved at the lowest growth temperature and with a carrier gas of 100% N_2. Efforts to further reduce the growth temperature to increase the nitrogen content resulted in very poor films without a clear defined DCXRD peak. Samples grown with 100% N_2 exhibit a similar temperature dependence for nitrogen incorporation as for those samples grown with 50% H_2/50% N_2, but also consistently show overall higher levels of nitrogen incorporation in the alloy.

Figure 2 shows the deterioration of surface morphology with increasing nitrogen content from 2.1 to 8.1%. The images are taken from an optical microscope at 40X magnification. All layers are sufficiently thick to be considered relaxed. The surface morphology for the GaAsN film with 2% nitrogen is essentially specular, while the surface takes on a cross hatched appearance for the sample with 4.9% nitrogen content. At 8.1% nitrogen content in GaAsN, the surface morphology has degraded significantly and becomes extremely rough.
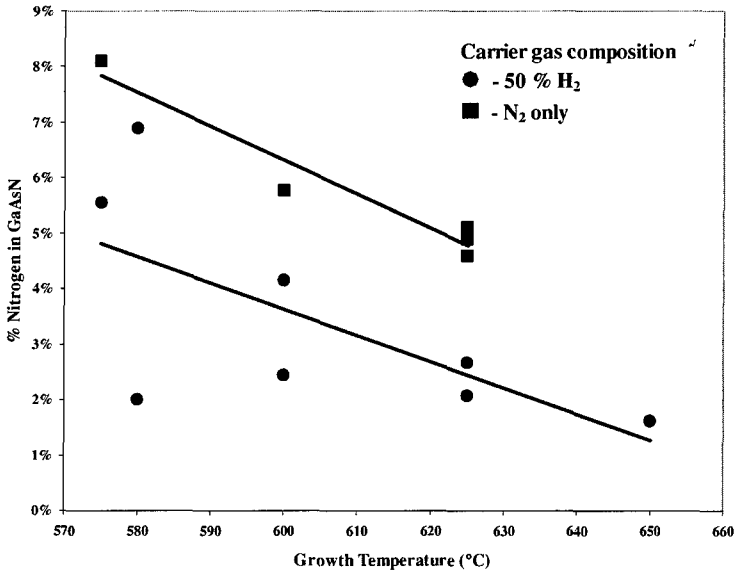

Figure 1. Percent nitrogen incorporation in thick GaAsN films vs. growth temperature (°C) for 50% H_2 in the carrier gas (●), and 0% H_2 (i.e., N_2 only) in the carrier gas (■).

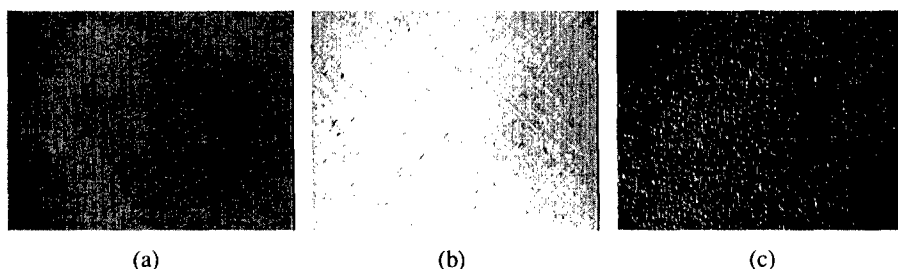(a)   (b)   (c)

Figure 2. Variation of surface morphology for thick GaAsN films with (a) 2.1, (b) 4.9, and (c) 8.1% nitrogen content.

Figure 3 shows 77K PL data for several GaAsN films, all grown at 625 °C, whose nitrogen content has essentially been determined by the percent H_2 in the carrier gas at this constant growth temperature during the growth process. The percent nitrogen incorporation in the films is 2.7, 3.5, and 5.0% grown with 50, 40, and 25% H_2 in the carrier gas respectively. The 77K PL data indicates a bandgap red shift from ~1.37 to ~1.23 eV. Interpretation of the PL spectrum and determination of the bandgap from PL measurements is more difficult for films with higher nitrogen content as the PL signal weakens and broadens with increasing nitrogen incorporation. The relatively poor DCXRD and PL data for $GaAs_{1-y}N_y$ films with high values of y can be the result of the deteriorated film quality, both optical and structural, with increasing nitrogen content in these metastable alloys. This is coupled with an increasing lattice mismatch between these relaxed GaAsN films and the GaAs substrate. The PL data and the deduced bandgap from this study indicate higher values of bandgap compared with other published data for strained films. This is due to the fact that PL is carried out at 77K and that the films in this study are thick and relaxed.
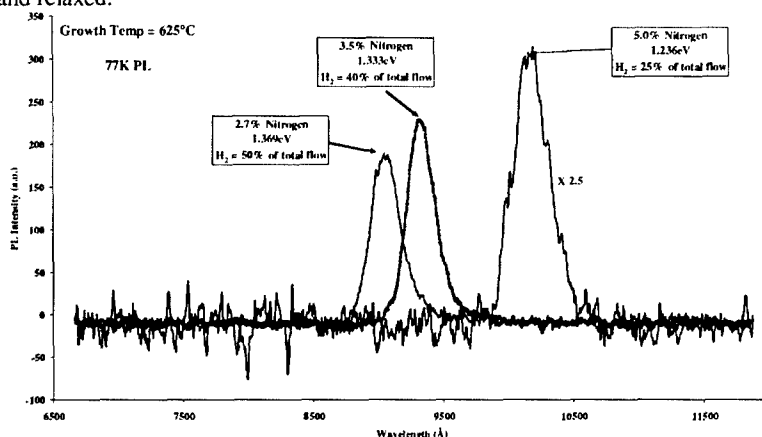

Figure 3. 77K PL for GaAsN films grown at 625 °C with nitrogen concentrations of 2.7, 3.5, and 5.0% grown with 50, 40, and 25% H_2 in the carrier gas respectively.

Figure 4 displays a plot of 77K bandgap determined from the PL peak emission of GaAsN for films grown at 600 °C. Over the composition range from ~3.5 to ~6% nitrogen a fairly linear relationship is indicated. Some discrepancy may exist between these values and other values reported in the literature due to the fact that these films are relatively thick and relaxed.
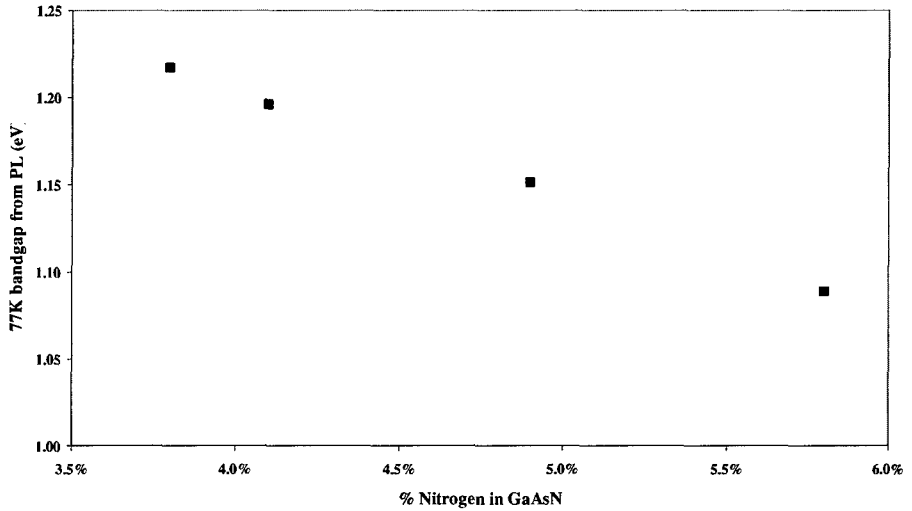

Figure 4. 77K bandgap vs. % Nitrogen content for thick GaAsN films

CONCLUSIONS

In conclusion, hydrogen has been shown to reduce the incorporation of nitrogen in GaAsN when present in the growth ambient during MOCVD. GaAsN films grown without H_2 in the growth ambient have exhibited N concentrations as high as 8.1 %. Variations in the nitrogen content in GaAsN as much as several percent have been measured when H_2 is used in the ambient in controlled amounts. A red shift and broadening of the PL is seen as the nitrogen content in these GaAsN films increases. The nature of the reduction of N in GaAsN in the presence of H_2 may include thermal and/or site-blocking effects.

ACKNOWLEDGEMENTS

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